$CsFe_3(PO_4)_3(OH_2)_2$: a Mixed-valence Iron Phosphate containing Trimeric Units of Iron–Oxygen Polyhedra*

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A mixed-valence iron phosphate, $CsFe_3(PO_4)_3(OH_2)_2$, has been synthesized hydrothermally and characterized by single-crystal X-ray diffraction and Mössbauer spectroscopy. The compound crystallizes in the monoclinic space group $C2/c$ with a = 13.435(2), b = 10.488(1), c = 9.024(2) Å, β = 108.60(1)°, U = 1205.1(3) Å^3 and Z = 4. The structure consists of a three-dimensional framework of vertex-sharing $Fe^{III}O_5$ trigonal bipyramids, $Fe^{II}O_4(OH_2)_2$ octahedra and PO_4 tetrahedra, enclosing a network of cavities, where the caesium cations reside. Mössbauer spectroscopy confirms the presence of one Fe^{II} and two Fe^{III}.

Iron phosphates have shown a rich crystal chemistry owing to the accessibility of more than one iron oxidation state and the ability of iron–oxygen polyhedra and phosphate tetrahedra to form a variety of network structures. These compounds often have complex crystal structures and present a challenge to complete structural characterization from a basic research point of view. The preparation of single crystals of iron phosphates calls upon several methods: hydrothermal growth, fluoride flux, vapour-phase transport, or simply prolonged heating.[1] We have recently synthesized a number of ternary iron phosphates using the hydrothermal technique, *viz.* $AFeP_2O_7$ (A = Rb or Cs),[2] $SrFe_3(PO_4)_3(HPO_4)$,[3] $CaFe_2(PO_4)_2(HPO_4)$,[4] $AFe_3(P_2O_7)_2$ (A = Sr or Ba),[5] $RbFe(HPO_4)_2$[6] and $AFe_5(PO_4)_5(OH)\cdot H_2O$ (A = Ca or Sr).[7] The structures of these phosphates cover discrete FeO_6 octahedra, FeO_5 trigonal bipyramids, dimers of corner-, edge- or face-sharing FeO_6 octahedra, and infinite chains of FeO_6 octahedra sharing either *trans* or skew edges. They include iron-(II), -(III) and mixed-valence compounds. Attempts to add new members to the system have yielded the mixed-valence iron phosphate $CsFe_3(PO_4)_3(OH_2)_2$. The framework contains trimers of corner-sharing Fe–O polyhedra forming $Fe_3O_{12}(OH_2)_2$ units. This paper reports the synthesis, single-crystal X-ray structure and Mössbauer spectroscopy of $CsFe_3(PO_4)_3(OH_2)_2$.

Experimental

Synthesis.—Crystals of $CsFe_3(PO_4)_3(OH_2)_2$ were obtained by heating a mixture of CsOH (0.940 g, 50%), $FePO_4\cdot 2H_2O$ (0.195 g), Fe (0.058 g), $(NH_4)_2HPO_4$ (0.276 g), H_3PO_4 (3 cm^3, 7.5 mol dm^{-3}), NMe_2H (1 cm^3, 40%) and water (7 cm^3) in a Teflon-lined autoclave (23 cm^3) at 230 °C for 5 d followed by slow cooling to room temperature. The product was filtered off, washed with water, rinsed with ethanol, and dried in a desiccator at ambient temperature. The product contained black crystals of $CsFe_3(PO_4)_3(OH_2)_2$ and a small amount of unknown colourless material. Although the role of NMe_2H and $(NH_4)_2HPO_4$ is not well understood, they appear crucial to obtain $CsFe_3(PO_4)_3(OH_2)_2$ as a major product under these conditions. Powder X-ray diffraction analysis on a powdered sample of manually selected black crystals agreed well with the calculated powder pattern based on the atomic coordinates from single-crystal X-ray diffraction data. Energy-dispersive X-ray fluorescence analysis on a black crystal showed that the Cs:Fe:P mole ratio was 0.93:3.07:3.00, in accord with the structural analysis. The sample was further characterized by thermogravimetric analysis under N_2 using a DuPont thermal analyser. It decomposed at about 400 °C and exhibited a weight loss of 5.48% at 500 °C. The weight loss corresponds to the loss of two water molecules and can be compared with the calculated value of 5.83%.

Mössbauer Spectroscopy.—The ^{57}Fe Mössbauer measurements were made on a constant-acceleration instrument. Velocity calibrations were made using 99.99% pure 10 μm iron foil. Typical linewidths for all three pairs of iron lines fell in the range 0.28–0.30 mm s^{-1}. Isomer shifts are reported with respect to iron foil at 300 K. It should be noted that the isomer shifts illustrated are plotted as experimentally obtained; tabulated data should be consulted.

Single-crystal X-Ray Diffraction.—A black parallelepiped crystal of dimensions 0.06 × 0.09 × 0.25 mm was used for indexing on an Enraf-Nonius CAD4 diffractometer with κ-axis geometry using monochromated Mo-Kα radiation. Unit-cell parameters were determined by a least-squares fit of 25 peak maxima having $15 < 2\theta < 34°$. Axial oscillation photographs were taken to check the cell parameters and symmetry properties. Of the 1460 reflections collected, 1264 unique reflections were considered observed $[I > 2.5\sigma(I)]$ after Lorentz polarization and empirical absorption corrections. Correction for absorption was based on φ scans of a few suitable reflections with χ values close to 90° using the NRC VAX program package.[8] Based on systematic absences, statistics of intensity distribution, and successful solution and refinement of the structure, the space group was determined to be $C2/c$. Direct methods (SHELXTL PLUS[9]) were used to locate the metal atoms with the remaining non-hydrogen atoms being found from successive difference maps. Bond-strength calculations were carried out to help locate any hydrogen atoms.[10] One oxygen atom was found to be considerably undersaturated; a valence sum of 0.37 was calculated for O(4). This value suggests that O(4) is a water oxygen. The hydrogen atoms were located from a difference map. Subsequent refinement, including the atomic coordinates for all atoms, anisotropic thermal parameters for all non-hydrogen atoms and fixed isotropic thermal parameters for hydrogen atoms, converged at R = 0.0198 and R' = 0.0241 $\{w = 1/[\sigma^2(F) + 0.000\,157F^2]\}$. The

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Crystallographic data and intensity-collection parameters for $CsFe_3(PO_4)_3(OH_2)_2$

Formula	$H_4CsFe_3O_{14}P_3$
M	621.40
Crystal system	Monoclinic
Space group	$C2/c$
a/Å	13.435(2)
b/Å	10.488(1)
c/Å	9.024(2)
β/°	108.60(1)
U/Å^3	1205.1(3)
Z	4
D_c/g cm^{-3}	3.425
F(000)	1176
μ(Mo-Kα)/cm^{-1}	70.2
T/°C	23
λ(Mo-Kα)/Å	0.709 30
Scan rate/° min^{-1}	5.49
Scan mode	θ–2θ
Scan width/°	$0.70 + 0.35 \tan\theta$
2θ Range/°	2–55
Standard reflections	Three measured every 60 min (no decay)
No. of reflections collected	1460
Unique observed reflections	1264 [$I > 2.5\sigma(I)$]
Parameters refined	98
R^a	0.0198
R'^b	0.0241
$(\Delta\rho)_{max,min}$/e Å^{-3}	0.68, −0.61

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R' = [w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$. Weighting scheme $w^{-1} = \sigma^2(F) + gF^2$, where $g = 0.000\,157$.

Table 2 Atomic coordinates for $CsFe_3(PO_4)_3(OH_2)_2$

Atom	X/a	Y/b	Z/c
Cs	0	0.358 25(3)	0.25
Fe(1)	0	0.718 41(6)	0.25
Fe(2)	−0.327 64(3)	0.424 68(4)	0.074 50(5)
P(1)	0	−0.008 4(1)	0.25
P(2)	0.207 95(6)	0.628 73(8)	0.171 0(1)
O(1)	−0.285 9(2)	0.584 6(2)	0.170 0(3)
O(2)	−0.224 0(2)	0.451 4(2)	−0.038 0(3)
O(3)	−0.057 8(2)	0.079 0(2)	0.115 0(3)
O(4)*	0.117 4(2)	0.296 6(3)	−0.016 5(3)
O(5)	−0.262 9(2)	0.268 7(2)	0.156 0(3)
O(6)	−0.426 3(2)	0.399 6(2)	0.202 0(3)
O(7)	0.095 1(2)	0.613 8(2)	0.166 7(3)

* Water oxygen atom.

caesium atom was allowed to refine and did not deviate significantly from full occupancy. Neutral-atom scattering factors for all atoms were used. Anomalous dispersion corrections were applied.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The crystallographic data are listed in Table 1. The atomic coordinates and selected bond distances, angles and bond-valence sums[10] are given in Tables 2 and 3 respectively. The Cs, Fe(1) and P(1) atoms sit on two-fold axes, all other atoms are located at general positions. The iron atoms are both five- and six-co-ordinated. The co-ordination number of Cs^+ was determined on the basis of the maximum gap in the Cs–O distances ranked in increasing order. The maximum cation–anion distance, L_{max}, according to Donnay and Allmann[11] was also considered. Therefore, the Cs atom is co-ordinated by 12 oxygen atoms and the thirteenth Cs–O bond length is 4.230 Å.

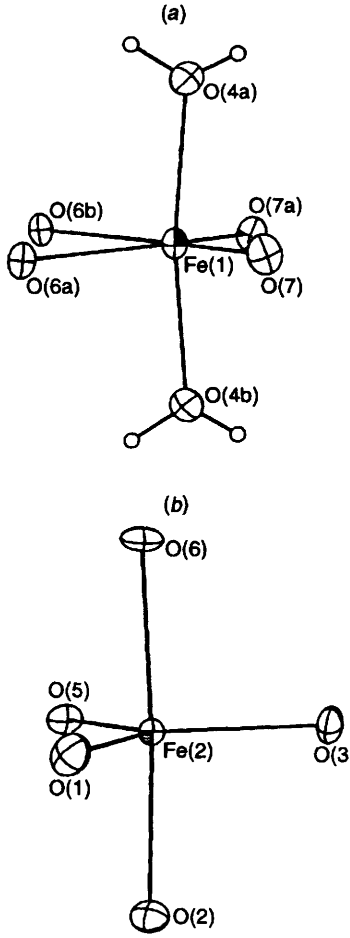

Fig. 1 The $FeO_4(OH_2)_2$ octahedron (*a*) and FeO_5 trigonal bipyramid (*b*) in $CsFe_3(PO_4)_3(OH_2)_2$. Thermal ellipsoids for Fe, P and O atoms are shown at the 60% probability level

Atom Fe(1) is octahedrally co-ordinated by four phosphate oxygen atoms and two *trans* water molecules [Fig. 1(*a*)]. The co-ordination polyhedron of Fe(2) is trigonal bipyramidal [Fig. 1(*b*)], co-ordination number five being less common than six in iron phosphates. The axial oxygens O(2) and O(6) bend slightly away from the equatorial oxygen O(3) and the O(2)–Fe(2)–O(6) angle decreases to 176.5°. The axial Fe(2)–O bonds are longer than the equatorial. Bond-length bond-strength calculations indicate that Fe(1) and Fe(2) are in the +2 and +3 states, respectively. Based on crystal-field theory, high-spin Fe^{2+} gains slightly more crystal-field stabilization energy in an octahedral site than in a trigonal-bipyramid site. In contrast, in the mixed-valence compound $CaFe_5(PO_4)_5(OH)(OH_2)$ the divalent iron has trigonal bipyramidal co-ordination and all trivalent irons have octahedral co-ordination.[7] In $CsFe_3(PO_4)_3(OH_2)_2$ the P–O bond lengths have average values of 1.533 Å for P(1) and 1.534 Å for P(2). The values are in agreement with the expected value of 1.53 Å predicted by Shannon.[12] Based on the distribution of P–O bond lengths, P(2) is within a more distorted tetrahedron than P(1). The P(2)–O(7) bond length is the shortest as O(7) is bonded to Fe^{2+}, and all other phosphate oxygens are bonded to Fe^{3+}. The P(2)–O(1) bond is the longest as O(1) is involved in stronger hydrogen bonding.

The structure of $CsFe_3(PO_4)_3(OH_2)_2$ is illustrated in Fig. 2. It adopts a new crystal structure, consisting of a three-dimensional framework of vertex-sharing FeO_5 trigonal bipyramids, $FeO_4(OH_2)_2$ octahedra and PO_4 tetrahedra, enclosing a network of cavities, where the Cs^+ cations reside. The cavities are connected through one-dimensional channels,

Table 3 Selected bond lengths (Å), angles (°) and bond-valence sums (Σs) for $CsFe_3(PO_4)_3(OH_2)_2$

Cs–O(2)	3.432(2) (2 ×)	Cs–O(3)	3.172(2) (2 ×)
Cs–O(4)	3.333(3) (2 ×)	Cs–O(5)	3.488(2) (2 ×)
Cs–O(7)	3.161(3) (2 ×)	Cs–O(7)	3.577(3) (2 ×)
Σs(Cs–O) = 1.02			
Fe(1)–O(4)	2.199(2) (2 ×)	Fe(1)–O(6)	2.248(3) (2 ×)
Fe(1)–O(7)	2.003(3) (2 ×)		
Σs[Fe(1)–O] = 2.03			
Fe(2)–O(1)	1.888(2)	Fe(2)–O(2)	1.988(3)
Fe(2)–O(3)	1.901(2)	Fe(2)–O(5)	1.888(2)
Fe(2)–O(6)	2.030(3)		
Σs[Fe(2)–O] = 2.91			
P(1)–O(3)	1.525(2) (2 ×)	P(1)–O(6)	1.541(3) (2 ×)
Σs[P(1)–O] = 5.02			
P(2)–O(1)	1.553(2)	P(2)–O(2)	1.535(3)
P(2)–O(5)	1.537(2)	P(2)–O(7)	1.513(3)
Σs[P(2)–O] = 5.00			
H(1)–O(4)	0.81	H(2)–O(4)	0.88
H(1)···O(2)	2.17	H(2)···O(1)	1.98
O(4a)–Fe(1)–O(4b)	171.8(2)	O(4a)–Fe(1)–O(6a)	95.8(1)
O(4a)–Fe(1)–O(6b)	91.1(1)	O(4a)–Fe(1)–O(7)	87.1(1)
O(4a)–Fe(1)–O(7a)	88.4(1)	O(7)–Fe(1)–O(6a)	91.0(1)
O(7)–Fe(1)–O(7a)	113.6(2)	O(6a)–Fe(1)–O(6b)	64.6(1)
O(2)–Fe(2)–O(1)	87.3(1)	O(2)–Fe(2)–O(3)	92.4(1)
O(2)–Fe(2)–O(5)	90.6(1)	O(2)–Fe(2)–O(6)	176.5(1)
O(1)–Fe(2)–O(3)	117.8(1)	O(1)–Fe(2)–O(5)	124.0(1)
O(3)–Fe(2)–O(5)	118.2(1)	O(6)–Fe(2)–O(1)	90.5(1)
O(6)–Fe(2)–O(3)	91.1(1)	O(6)–Fe(2)–O(5)	88.3(1)
Fe(1)–O(6)–Fe(2)	128.8(1)	H(1)–O(4)–H(2)	115.9

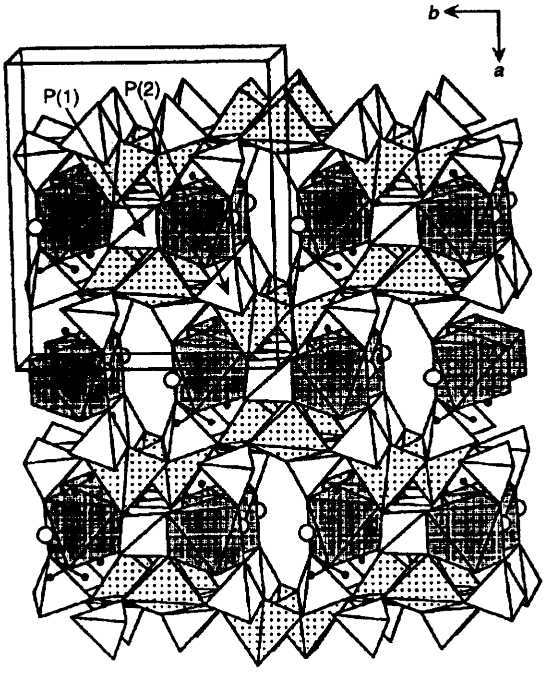

Fig. 2 Polyhedral view of $CsFe_3(PO_4)_3(OH_2)_2$ in a direction approximately parallel to the [001] direction. Large open and small solid circles are Cs and H atoms, respectively

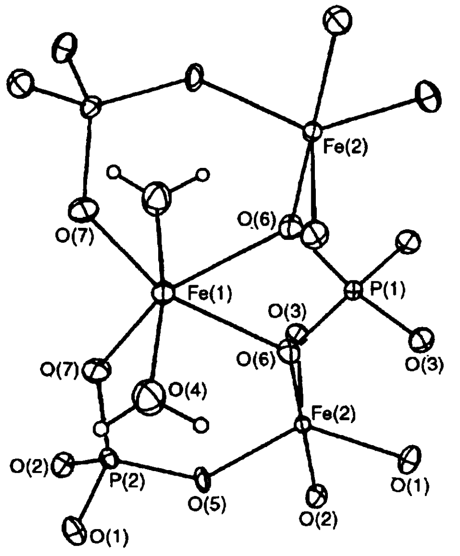

Fig. 3 A trimer formed from a corner-sharing $FeO_4(OH_2)_2$ octahedron and FeO_5 trigonal bipyramids. Thermal ellipsoids for Fe, P and O atoms are shown at the 60% probability level

aligned parallel to the *c* axis, *via* eight-ring windows. Each window is formed by the edges of two octahedra, two trigonal bipyramids and four tetrahedra. The building block of the structure may be viewed as one $FeO_4(OH_2)_2$ octahedron and two FeO_5 trigonal bipyramids linked *via* corners into a trimeric unit of composition $Fe_3O_{12}(OH_2)_2$ (Fig. 3). The Fe–O bonds involving the bridging oxygen, O(6), are the longest in their respective polyhedra. The Fe(1)–O(6)–Fe(2) bond angle is 128.8°. These trimeric units are connected by phosphate tetrahedra *via* corner and edge sharing. Each $P(1)O_4$ shares an edge with one $FeO_4(OH_2)_2$, and the remaining two corners with two FeO_5 trigonal bipyramids belonging to two adjacent trimeric units, such that infinite chains along the [001] direction are formed (Fig. 4). These infinite chains are further knitted together by $P(2)O_4$ tetrahedra *via* corner sharing to form a three-dimensional architecture. Each $P(2)O_4$ tetrahedron shares two corners with one $FeO_4(OH_2)_2$ and one FeO_5 within the same infinite chain, and the remaining two corners with two FeO_5 trigonal bipyramids belong to a neighbouring chain.

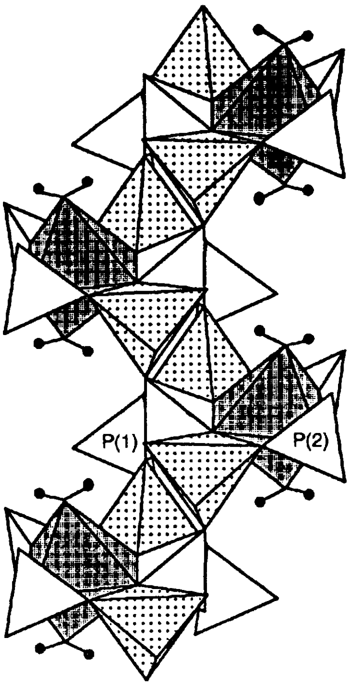

Fig. 4 Section of an infinite chain formed from trimeric units and phosphate tetrahedra as viewed along [100]

Table 4 Iron-57 Mössbauer least-squares fitting parameters (mm s^{-1}) for $CsFe_3(PO_4)_3(OH_2)_2$ at 300 K

	Intensity ratio	δ^a	$\Delta E_Q{}^b$	Γ^c
Component 1	1	1.23	2.75	0.28, 0.29
Component 2	2	0.35	0.28	0.34, 0.34

^{a} Isomer shift (referred to iron). ^{b} Quadrupole splitting. ^{c} Full width at half-height. The width for the line at more positive velocity is listed first for each doublet.

As shown in Fig. 5, the room-temperature Mössbauer spectrum of $CsFe_3(PO_4)_3(OH_2)_2$ can be described by the overlap of two symmetric doublets with constraint on the area ratio of 1 : 2. All the spectral parameters are listed in Table 4. Components 1 and 2 have isomer shifts consistent with those for Fe^{II} and Fe^{III} compounds as compiled by Gleitzer[1] and can be assigned Fe(1) and Fe(2), respectively. Thus the Mössbauer spectrum confirms the presence of one Fe^{II} and two Fe^{III} in $CsFe_3(PO_4)_3(OH_2)_2$.

A new mixed-valence iron phosphate, $CsFe_3(PO_4)_3(OH_2)_2$, has been prepared and structurally characterized. Iron phosphates exist as minerals and have a rich and complex structural chemistry. The structural diversity of this system is considerably expanded by the introduction of a variety of cations. Since the hydrothermal method is particularly suited for the synthesis and crystal growth of new crystalline phases, it is likely that many more iron phosphates with novel frameworks will be forthcoming.

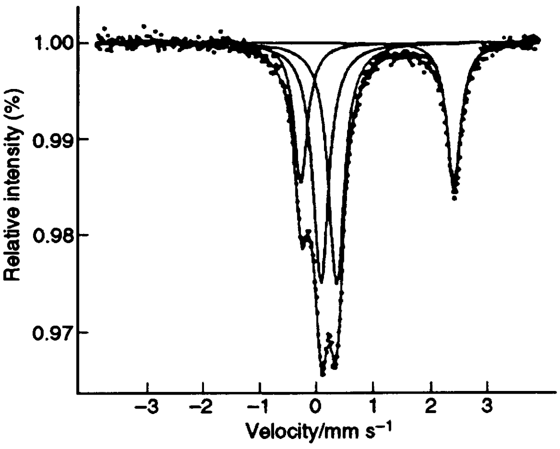

Fig. 5 Mössbauer spectrum of $CsFe_3(PO_4)_3(OH_2)_2$ at 300 K

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